

**(12) UK Patent Application**

**(19) GB**

**(11) 2 221 940**

**(13) A**

**(43) Date of A publication 21.02.1990**

**(21) Application No 8917892.5**

**(22) Date of filing 04.06.1989**

**(30) Priority data**

**(31) 232297**

**(32) 15.06.1988**

**(33) US**

**(51) INT CL<sup>4</sup>  
C09K 7/02**

**(52) UK CL (Edition J)  
E1F FGP**

**(56) Documents cited  
EP 0175412 A**

**(58) Field of search  
UK CL (Edition J) E1F FGP  
INT CL<sup>4</sup> C09K**

**(71) Applicant**

**Baroid Technology Inc**

**(Incorporated in the USA - Delaware)**

**3000 Sam Houston Parkway, Houston, Texas 77032,  
United States of America**

**(72) Inventor**

**James V. Fisk Jr**

**(74) Agent and/or Address for Service**

**Urquhart-Dykes & Lord  
91 Wimpole Street, London, W1M 8AH,  
United Kingdom**

**(54) Well drilling fluid and method of drilling employing said fluid**

**(57) A drilling fluid comprising an aqueous medium, a water-soluble cationic polymer, hydroxyethyl cellulose having a molecular weight of 3,000 to 40,000, and a generally water-insoluble weighting agent stabilizes shale formations, and exhibits good fluid loss control. Preferred cationic polymers (a) branched emulsion polymers of diallyldimethylammonium chloride having a molecular weight of at least 5,000, (b) dialkylaminoalkyl acrylic ester polymers, (c) dialkylaminoalkyl methacrylic ester polymers, (d) dialkylaminoalkyl acrylic acid-acrylamide copolymers, (e) dialkylaminoalkyl methacrylic acid-acrylamide copolymers, (f) N-(Dialkylaminoalkyl) acrylamide polymers, (g) N-(Dialkylaminoalkyl) methacrylamide polymers, (h) poly(2-vinylimidazoline), (i) poly(alkyleneamines), (j) poly(hydroxalkylene polyamines), and mixtures thereof.**

**GB 2 221 940 A**

**BEST AVAILABLE COPY**

**WELL DRILLING FLUID AND METHOD OF  
DRILLING EMPLOYING SAID FLUID**

The present invention relates to drilling fluids and, more particularly, to drilling fluids exhibiting good fluid loss control and stabilization of shale formations.

It is known that shale is predominantly formed of clays which swell and disperse when contacted with a water-based drilling fluid. This swelling and dispersion can result in a phenomenon known as "heaving", in which the borehole walls can collapse. To reduce this tendency of the clays in the shale to swell and disperse, it is common practice to add cationic salts to render the clays generally hydrophobic. When this is done, however, anionic polymers which are commonly used as viscosifiers in drilling fluids are also rendered hydrophobic, thereby losing their ability to viscosify the drilling fluid or mud and reduce fluid loss from the formation.

It is known to use mixtures of cationic polymers and high molecular weight hydroxyethyl cellulose (HEC) when drilling shale formations, in order to stabilize the shale by flocculating the clay, and to impart viscosification. Prior art cationic drilling mud systems containing HEC, however, suffer from the disadvantages of higher than desired fluid loss, and the inability effectively to suspend weighting agents, such as barite, at a viscosity which permits pumping of the fluid.

It would therefore be desirable to have a cationic polymer-based drilling fluid which would stabilize the shale, exhibit low fluid loss, viscosify, and effectively suspend weighting agents, such as barite.

The objects of the present invention are to provide an improved cationic polymer-based drilling fluids which will effectively suspend weighting agents, exhibit low fluid loss and stabilize shale formations.

The present invention provides a drilling fluid which comprises:

- (i) an aqueous medium,
- (ii) from 0.5 to 3.0 pounds per barrel (1.43 to 8.58 g/litre) of a water-soluble cationic polymer
- (iii) from 0.5 to 3.0 pounds per barrel (1.43 to 8.58 g/litre), based on aqueous medium, of hydroxyethyl cellulose having a molecular weight from 3000 to 4000, and
- (iv) from 1 to 300 pounds per barrel (2.86 to 8.58 g/litre), based on aqueous medium, of a generally water-insoluble weighting agent.

Preferably, the cationic polymer is:-

- (a) a branched emulsion polymer of diallyldimethylammonium chloride having a molecular weight of at least 5,000,
- (b) a dialkylaminoalkyl acrylic ester polymer,
- (c) a dialkylaminoalkyl methacrylic ester polymer,
- (d) a dialkylaminoalkyl acrylic acid-acrylamide copolymer,
- (e) a dialkylaminoalkyl methacrylic acid-acrylamide copolymer,
- (f) an N-(Dialkylaminoalkyl) acrylamide polymer,
- (g) an N-(Dialkylaminoalkyl) methacrylamide polymer,

- (h) a poly(2-vinylimidazoline),
- (i) a poly(alkyleneamine)
- (i) a poly hydroxalkylene polyamine) or a mixture thereof.

When the aqueous medium contains a salt of a multivalent cation, the drilling fluid will also contain a non-water-swellable clay which can be added to the drilling fluid before drilling, or can be picked up by the drilling fluid, *in situ*, during the drilling operation.

The present invention also provides a method of drilling wherein the drilling fluid described above is circulated in a borehole during the drilling operation.

The aqueous medium used in the drilling fluid compositions of the present invention can be fresh water, brines containing monovalent cations, such as sodium chloride solutions or potassium chloride solutions, brines containing multivalent cations, such as calcium chloride solutions, sea water etc. The nature of the aqueous medium, as seen hereafter, determines the composition of the drilling fluid.

The cationic polymers which are useful in the compositions and method of the present invention are those cationic polymers which will stabilize, i.e. prevent erosion or dispersion of, shale containing water-swellable clays, so as to prevent heaving during the drilling operation, which are substantially water-soluble, or dispersible in the aqueous medium, and which act effectively to suspend weighting agents, such as barite. The cationic polymers will be present in amounts ranging from 0.5 to 3 pounds per barrel (ppb) (1.43 to 8.58 g/litre) of the aqueous medium. Non-limiting examples of

suitable cationic polymers include:

- (a) branched emulsion polymers of diallyldimethylammonium chloride having a molecular weight of at least 5,000,
- (b) dialkylaminoalkyl acrylic ester polymers,
- (c) dialkylaminoalkyl methacrylic ester polymers,
- (d) dialkylaminoalkyl acrylic acid-acrylamide copolymers,
- (e) dialkylaminoalkyl methacrylic acid-acrylamide copolymers,
- (f) N-(Dialkylaminoalkyl) acry amide polymers,
- (g) N-(Dialkylaminoalkyl) methacrylamide polymers,
- (h) poly(2-viny imidazoline).
- (i) poly(alkyleneamines),
- (i) poly(hydroxalkylene polyamines), and mixtures thereof.

The diallyldimethylammonium chloride polymers useful according to the present invention can be homopolymers, or copolymers with other monomers, such as acrylamides. Preferably, the polymers are branched emulsion-type polymers which can employ branching agents such as triallylmethylammonium chloride or tetraallylammonium chloride, as well as bis-diallylammonium salts such as tetraallylpiperazinium chloride and N,N,N',N'-tetraallyl-N,N'-dimethylhexamethylenediammonium chloride. The emulsion polymers can be prepared by emulsion or suspension polymerization techniques, such as those described in US-A-3968037, and may contain from 95 to 99.99 mole percent of diallyldimethylammonium chloride and from 0.01 to 5 mole percent of one of the aforementioned branching agents. The branched emulsion polymers can have molecular weights of at least 5,000, and preferably from 40,000 to 5,000,000. Especially preferred are homopolymers of dimethyldiallylammonium chloride having a molecular weight from 1,000,000 to 5,000,000.

Other cationic polymers especially suitable for use in accordance with the present invention are N-(Dialkylaminoalkyl) acrylamide polymers, for example polymers prepared via the Mannich Reaction wherein a polyacrylamide is reacted with formaldehyde and an amine to produce an aminomethylated polyacrylamide. Especially preferred are such polyacrylamides having molecular weights from 40,000 to 4,000,000.

Another preferred type of cationic polymer for use in accordance with the present invention are the dialkylaminoalkyl derivatives of a water-soluble copolymer formed from an ethylenically unsaturated amide monomer and a comonomer selected from acrylic acids, alkyl-substituted acrylic acids and mixtures thereof, for example the copolymer of acrylamide and methacrylic acid. Such polymers, which can have molecular weights from 40,000 to 4,000,000, can be produced, for example, by the method described in US-A-3923756. A particularly preferred class of copolymer are the dialkylaminoalkyl acrylamide-methacrylic acid copolymers wherein the copolymer has a molecular weight from 40,000 to 4,000,000. Especially preferred, non-limiting examples of such copolymers include the dimethylaminoethyl sulphates and chlorides of copolymers of acrylamide and methacrylic acid.

It has been found that the molecular weight of the particular cationic polymer has very little effect on its ability to stabilize the shale or suspend the weighting agent. Thus, as noted above, cationic polymers of widely different molecular weights can be employed.

The compositions of the present invention also employ

hydroxyethyl cellulose (HEC) as a viscosifier and fluid loss control additive. The HEC, which will be present in the composition in amounts from 0.5 to 3 pounds per barrel, (1.43 to 8.58 g/litre), preferably 0.5 to 2.5 pounds per barrel, (1.43 to 7.15 g/litre), of the aqueous medium, must have a molecular weight from 3,000 to 40,000 depending upon the degree of viscosification desired. HEC having a higher molecular weight cannot be used to form weighted muds in the compositions of the present invention.

When the drilling fluid of the present invention contains a salt of a multivalent cation, e.g., calcium chloride or sea water, it is necessary in order to achieve acceptable fluid loss control, to include a non-water-swellable clay. Such clays can be dispensed with if the aqueous medium is fresh water, or contains only the salt of a monovalent cation, such as sodium chloride. The non-water-swellable clay can be added to the drilling fluid at the start of drilling if the formation through which the drilling progresses does not contain a non-water-swellable clay. Alternatively, the clay can be picked up, *in situ*, by the drilling fluid during the actual drilling operation, since many formations contain such non-water-swellable clays which form part of the drill cuttings. The non-swellable clay will normally be present in the drilling fluid in amounts from 1 to 15 pounds per barrel (2.86 to 42.9 g/litre) of the aqueous medium. Suitable, non-limiting examples of such non-water-swellable clays include kaolin, attapulgite and sepiolite.

The compositions of the present invention also include a water-insoluble weighting agent such as barite, although other weighting agents such as galena, hematite and other mineral materials may be employed. The weighting agent

will generally be present in the compositions in amounts of from 1 to 300 pounds per barrel (2.86 to 8.58 g/litre) of the aqueous medium.

The compositions of the present invention may contain other materials or additives, such as additional viscosifiers or fluid loss control additives or salts, to tailor the mud to desired needs.

In the method of the present invention, the drilling fluid, if the formation contains a non-water-swellable clay, is circulated in the well bore, the non-swellable clay being incorporated in situ into the drilling fluid. Alternatively, the drilling fluid having added non-swellable clay is circulated in the borehole during the drilling operation, this being the method utilized when the formation through which the borehole is being drilled is devoid of non-water-swellable clay.

To more fully illustrate the invention, the following non-limiting examples are presented.

#### EXAMPLE 1

A series of drilling muds of varying compositions were prepared and tested. In all instances, unless otherwise indicated in this and all the other Examples, the muds were prepared by mixing for 20 minutes on a Multimixer following by rolling for 16 hours at 150°F (65.5°C) before testing. The compositions of the drilling fluids, and test results are shown in Table 1 below.

TABLE 1

<u>Formulation</u>	Mud No. 1	Mud No. 2	Mud No. 3	Mud No. 4	Mud No. 4a	Mud No. 4b
TAP WATER, bbl (litre)	0.75 (86.7)	0.75 (86.7)	0.75 (86.7)	0.75 (86.7)	0.75 (86.7)	0.75 (86.7)
KCl, lb (Kg)	21 (9.5)	21 (9.5)	21 (9.5)	21 (9.5)	21 (9.5)	21 (9.5)
LV 214, 283 E <sup>1</sup> , lb (Kg)	1 (0.45)	1 (0.45)	1 (0.45)	1 (0.45)	1 (0.45)	1 (0.45)
HBC-QP <sup>2</sup> , 300, lb (Kg)	1.5 (0.63)	3.0 (1.63)	— —	— —	— —	— —
HBC-QP <sup>3</sup> , 4400, lb (Kg)	— —	1.5 (0.63)	3.0 (1.36)	— —	— —	— —
ZB0GEL <sup>4</sup> , 1b (Kg)	10 (4.54)	10 (4.54)	10 (4.54)	10 (4.54)	10 (4.54)	10 (4.54)
XC Polymer, 1b (Kg)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)
BAROID <sup>5</sup> , 1b (Kg)	200 (90.72)	200 (90.72)	200 (90.72)	200 (90.72)	200 (90.72)	200 (90.72)
Kaolin, 1b (Kg)	— —	— —	— —	— —	— —	— —
BABASING DAFORM <sup>6</sup> , 1b (Kg)	0.2 (0.09)	0.2 (0.09)	0.2 (0.09)	0.2 (0.09)	0.2 (0.09)	0.2 (0.09)
Plastic Viscosity, cP	15 1b/100 sq ft (Pa)	18 (22.97)	23 (29.24)	Too Thick	47 (25.06)	16 (27.15)
10-sec gel, 1b/100 sq ft (Pa)	11 (22.97)	14 (8.35)	12 (12.53)	To Mix	3 (6.27)	4 (10.44)
10-min gel, 1b/100 sq ft (Pa)	45 (93.98)	19 (39.68)	40 (83.54)	To On	7 (14.62)	7 (14.62)
Fluid Temperature, °F (°C)	74 (23)	74 (23)	74 (23)	74 Multi Mixer	74 (23)	74 (23)
pH	8.4 (8.4)	8.4 (8.4)	8.4 (8.4)	Multi Mixer	8.0 8.2	7.8 50+
API Fluid Loss, ml	16	12.5	6.0	—	—	—
Mud wt, lb/gal (g/cm <sup>3</sup> )	13.0 (1.56)	13.0 (1.56)	13.0 (1.56)	—	—	—

<u>Formulation</u>	Mud <u>No. 5</u>	Mud <u>No. 6</u>	Mud <u>No. 7</u>	Mud <u>No. 8</u>	Mud <u>No. 9</u>	Mud <u>No. 10</u>
Tap water, bbl (litre)	0.75 (86.7) 21	0.75 (86.7) 21	0.70 (80.9) 21	0.70 (80.9) 21	0.70 (80.9) 21	0.65 (75.1) 21
KCl, 1b (Kg)	( 9.5) 1					
LV 214, 283 El, 1b (Kg)	( 0.45) 3.0 ( 1.36)	( 0.45) 3.0 ( 1.36)	( 0.45) 1.0 ( 0.45)	( 0.45) 1.5 ( 0.63)	( 0.45) 3.0 ( 1.36)	( 0.45) 3.0 ( 1.36)
HEC-QP3, 4400, 1b (Kg)	-	-	-	-	-	-
ZEOGEL <sup>4</sup> , 1b (Kg)	200 ( 90.72)	200 ( 90.72)	300 (136.1)	300 (136.1)	300 (136.1)	400 (181.4)
BARABRINE DEPOAM <sup>6</sup> , 1b (Kg)	10 0.2 ( 0.09)	20 0.2 ( 0.09)				
Plastic Viscosity, cP	37	42	17	20	56	83
Yield Point, 1b/100 sq ft (Pa)	6 (12.53)	10 (20.89)	5 ( 10.44)	10 ( 20.89)	19 ( 39.68)	37 ( 77.28)
10-sec gel, 1b/100 sq ft (Pa)	2 ( 4.18)	2 ( 4.18)	4 ( 8.35)	4 ( 8.35)	3 ( 6.27)	4 ( 4.35)
10-sec gel, 1b/100 sq ft (Pa)	3 ( 6.27)	3 ( 6.27)	7 ( 14.62)	7 ( 14.62)	4 ( 8.35)	7 ( 14.62)
Fluid Temperature °F (°C)	74 (23)	74 (23)	74 (23)	74 (23)	74 (23)	74 (23)
pH	8.4 8.4 4.6	8.4 7.4 5.0	7.4 1.1 7.2	7.4 1.0 5.2	7.4 3.0 4.8	7.4 3.0 4.8
API Fluid Loss, ml	13.0 ( 1.56)	13.0 ( 1.56)	14.5 (1.74)	14.5 (1.74)	16.0 (1.92)	16.0 (1.92)
Mud wt, lb/gal (g/cm)						

- 10-
1. Aqueous solution of 7.7 molar (cationic activity) of dimethylaminooethyl sulphate salt of acrylamide-methacrylic acid copolymers having a molecular weight of 4,000,000).
  2. HEC marketed by Union Carbide having a molecular weight of 3,000.
  3. HEC marketed by Union Carbide having a molecular weight of 40,000.
  4. Non-water-swellable clay marketed by NL Baroid, Inc.
  5. Barite weighting agent marketed by NL Baroid, Inc.
  6. Mud defoamer marketed by NL Baroid, Inc.
  7. Heteropolysaccharide marketed by Kelco Rotary.

As can be seen from the data in Table 1, the drilling fluids of the present invention exhibit excellent rheological properties and fluid loss control. With reference to Mud No. 4, it can be seen that when too much HEC having a higher molecular weight, e.g., 40,000, is present, the drilling fluid becomes unacceptably thick. Indeed, it has been found that using HEC having molecular weights of several million makes it virtually impossible to formulate an acceptable drilling fluid containing a water-insoluble weighting agent. Although Mud No. 4a shows acceptable rheological properties, it has been found that it shows very poor shale stability, indicating the necessity of the presence of the cationic polymer to achieve shale stability. Note that when the HEC is not present (Mud No. 4b), there is virtually no fluid loss control. The data in Table 1 also demonstrate that the weighted muds can contain up to 400 pounds per barrel (1144 g/litre) of the weighting agent and still be an acceptable drilling fluid. It is to be noted, however, (See Mud No. 10) that the yield point of such heavily weighted mud is higher than would normally be desired.

EXAMPLE 2

Several drilling fluid formulations were prepared and tested. The compositions of the muds and the test results are shown in Table 2 below.

TABLE 2

<u>Formulation</u>	Mud <u>No. 1</u>	Mud <u>No. 2</u>
Tap water, bbl (litres)	0.7 (80.9)	0.7 (80.9)
Sea Salt, lb (Kg)	11 ( 4.99)	11 ( 4.99)
LV214 283 E, lb (Kg)	1 ( 0.45)	1 ( 0.45)
HEC-10, lb (Kg)	-	-
HEC-QP300, lb (Kg)	3.0 ( 1.36)	3.0 ( 1.36)
BAROID, lb (Kg)	300 (136.2)	300 (136.2)
XC Polymer, lb (Kg)	-	-
ZEOGEL, lb (Kg)	-	15 ( 6.81)
BARABRINE DEFOAM, lb (Kg)	0.2 (0.09)	.2 (Kg)
Premix (1 bbl(115.6 litres)		
Tap Water 100 lb (45.4 Kg)		
Kaolin, bbl litres)	-	-
Plastics Viscosity, cP	60	54
Yield Point,		
lb/100 sq ft (Pa)	22 (45.95)	21 (43.86)
10-sec gel,		
lb/100 sq ft (Pa)	3 ( 6.27)	4 ( 8.35)
10-min gel		
lb/100 sq ft (Pa)	4 ( 8.35)	7 (14.62)
Fluid Temperature, °F (°C)	74 (23)	74 (23)
pH	7.5	7.4
API Fluid Loss, lml	50±	6.0
Mud wt, lb/gal (g/cm³)	14.5 (1.74)	14.5 (1.74)

This example shows that when salts of multivalent cations, such as are contained in sea salt are present, a non-water-swellable clay must be present in order for the

drilling fluid to exhibit acceptable fluid loss properties. As can be seen, when no ZEOGEL is present (Mud No. 1), there is virtually no fluid loss control. The results in Table 2 are to be contrasted with the results in Table 1, wherein the aqueous medium contains only a salt having a monovalent cation (KCl) and wherein acceptable fluid loss control could be achieved even in the absence of any non-water-swellable clay (see Mud No. 9 in Table 1).

EXAMPLE 3

A series of drilling fluids were prepared by mixing the ingredients for 20 minutes on a multimixer. The drilling fluids were then hot rolled for 16 hours at 150°F (65.5°C) and tested. The compositions of the muds and the test results are shown in Table 3 below.

TABLE 3

<u>Formulation</u>	<u>Mud No. 1</u>	<u>Mud No. 2</u>	<u>Mud No. 3</u>	<u>Mud No. 4</u>	<u>Mud No. 5</u>
Tap water, bbl (litre)	0.75 (86.7)	0.75 (86.7)	0.70 (80.9)	0.70 (80.9)	0.70 (80.9)
KCl, 1b (Kg)	21 ( 9.5)	21 ( 9.5)	21 ( 9.5)	21 ( 9.5)	21 ( 9.5)
LV 214, 283 E <sup>1</sup> , 1b (Kg)	1 ( 0.45)	1 ( 0.45)	1 ( 0.45)	1 ( 0.45)	1 ( 0.45)
HEC QP <sup>2</sup> 300, 1b (Kg)	3.0 ( 1.36)	3.0 ( 1.36)	3.0 ( 0.45)	3.0 ( 0.45)	3.0 ( 1.36)
HBC-QP <sup>3</sup> , 4400, 1b (Kg)	-	-	-	-	-
ZBOGLEL <sup>4</sup> , 1b (Kg)	-	-	-	-	-
XC Polymer, 1b (Kg)	-	-	-	-	-
BAROID <sup>5</sup> , 1b (Kg)	200 ( 90.72)	200 ( 90.72)	300 (136.1)	300 (136.1)	300 (136.1)
Kaolin, 1b (Kg)	10 ( 0.09)	20 ( 0.09)	20 ( 0.09)	20 ( 0.09)	20 ( 0.09)
BARABRINE DSFOAM <sup>6</sup> , 1b (Kg)	0.2 ( 0.09)	0.2 ( 0.09)	0.2 ( 0.09)	0.2 ( 0.09)	0.2 ( 0.09)
Plastic Viscosity, cP	37 lb/100 sq ft (Pa)	42 (20.89)	17 (10.44)	20 (20.89)	56 (39.68)
Yield Point, lb/100 sq ft (Pa)	6 (12.53)	10 (20.89)	5 (10.44)	10 (20.89)	19 (39.68)
10-sec gel, 1b/100 sq ft (Pa)	2 (4.18)	2 ( 4.18)	4 ( 8.35)	4 ( 8.35)	3 ( 6.27)
10-sec gel, 1b/100 sq ft (Pa)	3 ( 6.27)	3 ( 6.27)	7 (14.62)	7 (14.62)	4 ( 8.35)
Fluid Temperature $\sigma_F$ ( $^{\circ}$ C)	74 (23)	74 (23)	74 (23)	74 (23)	74 (23)
pH	8.4 4.6	8.4 5.0	7.4 11	7.4 11	7.4 11
API Fluid Loss, ml	4.6 13.0	5.0 13.0	-	-	-
Mud wt, 1b/gal (g/cm <sup>3</sup> )	( 1.56)	( 1.56)	14.5 (1.74)	14.5 (1.74)	14.5 (1.74)

1/4

TABLE 3

<u>Formulation</u>	<u>Mud No. 6</u>	<u>Mud No. 7</u>	<u>Mud No. 8</u>	<u>Mud No. 9</u>	<u>Mud No. 10</u>
Tap water, bbl (litre)	0.70 (80.7)	0.70 (80.7)	0.70 (80.9)	0.70 (80.9)	0.70 (80.9)
KCl, 1b (Kg)	-	21 (9.53)	21 (9.53)	-	-
NaCl, 1b (Kg)	-	-	-	-	-
Seasalt, 1b (Kg)	11 (4.9)	-	-	11 (4.9)	11 (4.9)
E-9051 1b (Kg)	-	1 (0.45)	-	1 (0.45)	-
E-9042 1b (Kg)	1 (0.45)	-	1 (0.45)	-	1 (0.45)
HBC-QP 300, 1b (Kg)	3 (1.36)	-	-	-	-
ZEOGEL, 1b (Kg)	15 (6.81)	15 (6.81)	15 (6.81)	15 (6.81)	15 (6.81)
BAROID, 1b (Kg)	300 (136.2)	300 (136.2)	300 (136.2)	300 (136.2)	300 (136.2)
XC Polymer, 1b (Kg)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)	0.25 (0.11)
Mud Temperature $^{\circ}F$ ( $^{\circ}C$ )	75	75	75	75	75
Plastic Viscosity, cp	50	15	11	14	9
Yield Point, lb/100 sq ft (Pa)	40 (83.54)	35 (73.10)	54 (112.76)	36 (75.19)	41 (85.63)
10-sec gel, 1b/100 sq ft (Pa)	27 (56.39)	20 (41.77)	24 (50.13)	24 (50.13)	22 (45.95)
10-sec gel, 1b/100 sq ft (Pa)	67 (139.93)	22 (45.95)	27 (56.39)	22 (45.95)	20 (41.77)
pH	7.7	7.6	7.5	7.6	7.5
API Fluid Loss, ml	13.5	50+	50+	50+	50+
Mud wt, 1b/gal (g/cm <sup>3</sup> )	14.5 (1.74)	14.5 (1.74)	14.5 (1.74)	14.5 (1.74)	14.5 (1.74)

- 16 -
1. Trademark of an aqueous solution of 20 molar percent (cationic activity) of a homopolymer of dimethyldiallyl ammonium chloride having a molecular weight of 40,000 and marketed by Calgon Corp.
  2. Trademark of an aqueous solution of 15 molar percent cationic activity) of a homopolymer of dimethyldiallyl ammonium chloride having a molecular weight of 2,000,000 and marketed by Calgon Corp.

As can be seen from the data in Table 3, drilling fluids made in accordance with the present invention have excellent rheological properties and exhibit good fluid loss control. Note that when there is no low molecular weight HEC (Mud Nos. 7-10), there is essentially no fluid loss control.

EXAMPLE 4

To demonstrate that the drilling fluids of the present invention are effective in stabilizing shale, a series of drilling fluids was prepared and compared with a conventional prior anionic polymer-based drilling mud commonly used where shale stabilization is important. In testing the ability of the drilling fluids to stabilize the shale, Pierre shale samples weighing 15 grams and having a diameter between 0.08 and 0.19 inches (1.8 and 4.3 mm) were hot rolled at 150°F (65.5°C) over a six day period. The shale sample was removed from each drilling fluid and re-weighed periodically to determine the amount of erosion that was occurring. The mud compositions and test data are shown in Table 4 below.

<u>Formulation</u>	<u>Mud No. 1</u>	<u>Mud No. 2</u>	<u>Mud No. 3</u>	<u>Mud No. 4</u>	<u>Mud No. 5</u>
Tap water, bbl (litre)	1 (115.6)	1 (115.6)	1 (115.6)	1 (115.6)	1 (115.6)
KCl, 1b (Kg)	25 ( 11.35)				
KOH, 1b (Kg)	0.5 ( 0.23)				
HBC-QP 300, 1b (Kg)	3.0 ( 1.36)	- ( 0.45)	- ( 0.45)	- ( 0.68)	- ( 0.68)
E-905, 1b (Kg)	1 ( 0.45)	- ( 0.45)	- ( 0.45)	- ( 0.45)	- ( 0.45)
Drispac <sup>1</sup> b (Kg)	-	-	1.5 ( 0.45)	- ( 0.45)	- ( 0.45)
PAC-L <sup>2</sup> b (Kg)	-	-	1.0 ( 0.45)	1.5 ( 0.60)	- ( 0.60)
EZ-MUD <sup>3</sup> b (Kg)	-	-	1 ( 0.45)	1 ( 0.45)	1 ( 0.45)
THERM-CHEK <sup>4</sup> b (Kg)	-	-	3 ( 1.36)	- ( 0.45)	- ( 0.45)
Kaolin, 1b	10 ( 4.54)	10 ( 4.54)	5 ( 2.27)	10 ( 4.54)	10 ( 4.54)
8 erosion values at various times					
6 hrs	0	0	0	0	0
24 hr	9.0	9.2	15.5	28.5	15.2
48 hr	27.4	29.2	53.5	53.6	38.9
72 hr	47.0	47.8	73.5	70.1	55.2
144 hr	77.4	-	89.3	88.6	78.5

- 18 -

- 1 Trade name of carboxymethyl cellulose marketed by NL Baroid, Inc.
- 2 Trademark of a low molecular weight carboxymethyl cellulose marketed by NL Baroid, Inc.
- 3 Trade name of a partially hydrolyzed polyacrylamide (anionic polymer) marketed by NL Baroid, Inc.
- 4 Trademark of a sulfonated acrylamide copolymer marketed as a fluid loss additive by NL Baroid, Inc.

Mud No. 2 is a commonly used prior art anionic polymer-based drilling fluid used in drilling shale formations. While as can be seen, Mud No. 2 shows acceptable shale stabilization, it cannot be effectively weighted with weighting agents, such as barite or other generally non-

water-soluble weighting agents. On the other hand, Mud No. 1, made in accordance with the present invention, is equally as effective at shale stabilization and, as shown by previous data, can be easily weighted with barite. As can also be seen, drilling fluids which contain neither the cationic polymer nor HEC are not effective at stabilizing the shale (see Mud No. 3 and Mud No. 4). It can also be seen (Mud No. 5) that unless both the cationic polymer and the low molecular weight HPC are present, the drilling fluids are not as effective in stabilizing the shale, even in the presence of an anionic polymer commonly used for shale stabilization.

It can thus be seen that the drilling fluids of the present invention are effective at shale stabilization, exhibit low fluid loss and can be easily weighted with commonly used, generally water-insoluble weighting agents such as barite.

**CLAIMS**

1. A drilling fluid which comprises:

- (i) an aqueous medium,
- (ii) from 0.5 to 3.0 pounds per barrel (1.43 to 8.58 g/litre) of a water-soluble cationic polymer,
- (iii) from 0.5 to 3.0 pounds per barrel (1.43 to 8.58 g/litre), based on aqueous medium, of hydroxyethyl cellulose having a molecular weight from 3000 to 40000, and
- (iv) from 1 to 300 pounds per barrel (2.86 to 858 g/litre), based on aqueous medium, of a generally water-insoluble weighting agent.

2. A drilling fluid as claimed in Claim 1 wherein the cationic polymer is:

- (a) a branched emulsion polymer of diallyldimethylammonium chloride having a molecular weight of at least 5,000,
- (b) a dialkylaminoalkyl acrylic ester polymer,
- (c) a dialkylaminoalkyl methacrylic ester polymer,
- (d) a dialkylaminoalkyl acrylic acid-acrylamide copolymer,
- (e) a dialkylaminoalkyl methacrylic acid-acrylamide copolymer,

- (f) an N-(Dialkylaminoalkyl) acrylamide polymer
- (g) N-(Dialkylaminoalkyl) methacrylamide polymer
- (h) a poly(2-vinylimidazoline),
- (i) a poly(alkyleneamine),
- (j) a poly(hydroxalkylene polyamine) or a mixture thereof.

3. A drilling fluid as claimed in Claim 2 wherein the branched emulsion polymer (a) has a molecular weight of 40,000 to 5,000,000.

4. A drilling fluid as claimed in Claim 2 or 3 wherein the branched emulsion polymer, (a) is obtained from 95 to 99.99 mole percent of diallylmethylammonium chloride and from 0.01 to 5 mole percent of triallylmethylammonium chloride, tetraallyl ammonium chloride, tetraallylpiperazinium chloride or N,N,N',N-tetraallyl-N,N'-dimethylhexamethylenediammonium chloride as branching agent.

5. A drilling fluid as claimed in Claim 1 wherein the water-soluble cationic copolymer comprises a dimethylaminoalkyl acrylamide-methacrylic acid copolymer.

6. A drilling fluid as claimed in Claim 5 wherein the molecular weight of the dimethylaminoalkyl acrylamide-methacrylic acid copolymer is from 40,000 to 4,000,000.

7. A drilling fluid as claimed in any one of the preceding claims wherein the weighting agent comprises barite.

8. A drilling fluid as claimed in any one of the preceding Claims wherein the aqueous medium contains a salt of a monovalent cation.

9. A drilling fluid as claimed in any one of Claims 1 to 7 wherein the aqueous medium contains a salt of a multivalent cation and the drilling fluid contains a non-water-swellable clay.

10. A drilling fluid as claimed in Claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

11. A method of drilling an earth borehole in which a drilling fluid is circulated within the borehole, wherein the drilling fluid is a fluid according to any one of the preceding claims.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

**THIS PAGE BLANK (USPTO)**